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THE ROLE OF SULFIDE IN PREVENTING HEAVY METAL TOXICITY IN ANAEROBIC TREATMENT

Alonzo William Lawrence, et al

Stanford University
Stanford, California

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Alonzo Wm. Lawrence and Perry L. McCarty

Research Assistant and Associate Professor
of Sanitary Engineering, Stanford University

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The successful stabilization of organic wastes by the anaerobic waste treatment process has been shown to depend on the maintenance of an environment favorable to the organisms involved. The control or elimination of toxic materials is of major importance in maintaining such a favorable environment. In the realm of toxicity producing materials, "heavy metals" have long been known to cause retardation or complete cessation of the anaerobic process. In particular, copper and zinc originating from electroplating baths have been implicated in several treatment failures. Reported toxic concentrations of these materials have varied widely. For many years there was no rational scientific basis for explaining these variations or preventing the toxic effects, other than keeping the toxic materials out of the treatment system.

Recently, however, Masselli, Masselli and Burford[1] have reported that the toxic effects of copper could be eliminated by the addition of sulfide to the digester in stoichiometrically equivalent amounts. It was desired to assess the generality of their report, both with regard to high concentrations of copper and the use of sulfides for control of toxicity of other heavy metals. To this end, this study was performed to evaluate the use and importance of sulfide in the control of toxicity produced by the heavy metals copper, zinc, nickel, and iron in the anaerobic treatment of primary municipal sludge.

PREVIOUS STUDIES

The effects of copper, zinc, nickel, and iron on anaerobic waste treatment have received considerable attention in the past, as evidenced by numerous reports in the literature. Masselli et al[1] presented an excellent literature review of the occurrence of copper and zinc in domestic sewage and sewage sludge. In laboratory experiments they found copper concentrations of 150 to 500 mg/l or 0.5 to 1.7 percent by weight on a dry volatile solids basis adversely affected digestion.

A recent series of studies dealing with the effects of heavy metals on both aerobic and anaerobic treatment processes has been conducted by the personnel of the Robert A. Taft Sanitary Engineering Center of the U.S. Public Health Service. In addition to a report,[2] summarizing the results of these studies, individual reports have been presented on the effects on treatment units of copper,[3] zinc,[4] and nickel.[5] In all cases, toxic effects were related to the concentration of heavy metals in the raw sewage.

In several other investigations,[6][7][8][9] copper was reported to exert toxic effects on the anaerobic waste treatment process, while in another case,[10] high concentrations were reported to be non-toxic. In one laboratory study[11] nickel concentrations greater than 500 mg/l were found to cause retardation of the digestion process. Also, different forms and concentrations of iron have been shown[12][13] to variously aid and retard digestion.

In summary, previous studies indicate that high concentrations of heavy metals can cause rapid toxicity and cessation of the digestion process. Toxic concentrations reported, however, even for the same metal, have varied widely. The best explanation for these variations may be related to the different quantities of sulfide present in digesters as proposed for copper by Masselli, et al.[1]

THEORETICAL CONSIDERATIONS

The toxicity of heavy metals depends upon their concentration in the soluble or ionic form, and not upon the total concentration in the digester. Thus, effective removal of metal ions from the soluble phase, and hence from the biological environment should be effective in preventing toxicity to the organisms responsible for the anaerobic process. The role that sulfide can play in such a scheme of detoxification is illustrated by a consideration of the solubility of metal sulfides.

Metallic Sulfide Solubility

The presence or addition of sulfide to a digester containing heavy metals results in the formation of the corresponding metal sulfides which are extremely insoluble salts as illustrated by the solubility and solubility products given in Table 1.

TABLE 1

SOLUBILITY OF HEAVY METAL SULFIDES AT 18°C. (14)

Heavy Metal	Sulfide Salt	Solubility Product	Solubility mg/l
Copper	Cu_2S	2.0×10^{-47}	3×10^{-11}
Copper	CuS	8.5×10^{-45}	9×10^{-18}
Lead	PbS	3.4×10^{-28}	4×10^{-9}
Cobalt	CoS	3.0×10^{-26}	2×10^{-8}
Nickel	NiS	1.4×10^{-24}	1×10^{-7}
Zinc	ZnS	1.2×10^{-23}	3×10^{-7}
Iron	FeS	3.7×10^{-19}	5×10^{-5}

Copper is one of the most insoluble of the heavy metal sulfides, while iron is one of the least. However, in all cases the presence of sulfide for the formation of the corresponding metal sulfide should effectively reduce the soluble metal concentration to a value well below its toxic limit.

Sulfide Sources and Interactions

The sulfide necessary to effect the formation of a metallic sulfide precipitate in digesting sludge can originate from several sources. It may be introduced along with the raw waste, biologically produced in the digester by the reduction of sulfates or other sulfur-containing inorganic compounds, or released from the degradation of sulfur-containing organic materials such as proteins. The latter two probably account for the major portion of sulfides naturally occurring in sewage sludge digestion. The variability of sulfide content of digesting sludges is probably primarily related to the widely differing content of sulfates in raw sludges. A schematic representation of the interactions of sulfides in a digester is shown in Figure 1.

EXPERIMENTAL PROCEDURE

The experimental portion of this study was conducted (1) to determine the effects of various concentrations of copper, zinc, nickel and iron, both singly and in combination on anaerobic treatment, and (2) to investigate the postulated role of sulfide in preventing heavy metal toxicity. It was desired to have the experimental conditions simulate modern full-scale digester operation as closely as possible. To achieve this, a series of 1.5-liter laboratory digesters connected as shown in Figure 2 were operated on a 20-day detention time at 35°C. The digesters were mounted on a shaking platform to obtain continual mixing of the digester contents. The gas produced was collected for measurement over an acidified salt solution and expelled daily. The digesters were fed with primary sludge from the Menlo Park, California, municipal waste treatment plant. The sludge was diluted approximately 1:1 with tap water. A volume of mixed digester contents equal to the sludge addition volume of 75 ml was withdrawn daily for analysis. The average characteristics of the raw sludge feed during this study are shown in Table 2.

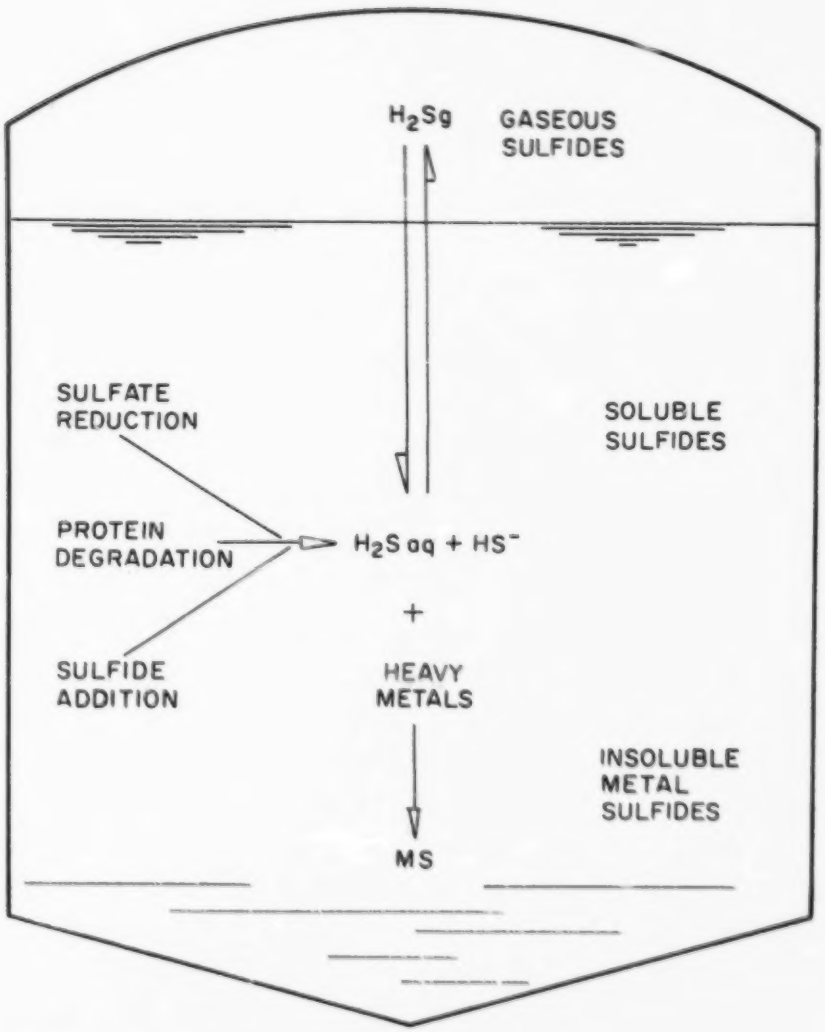


FIGURE - 1 - SCHEMATIC REPRESENTATION OF SULFIDE INTERACTIONS IN A DIGESTER

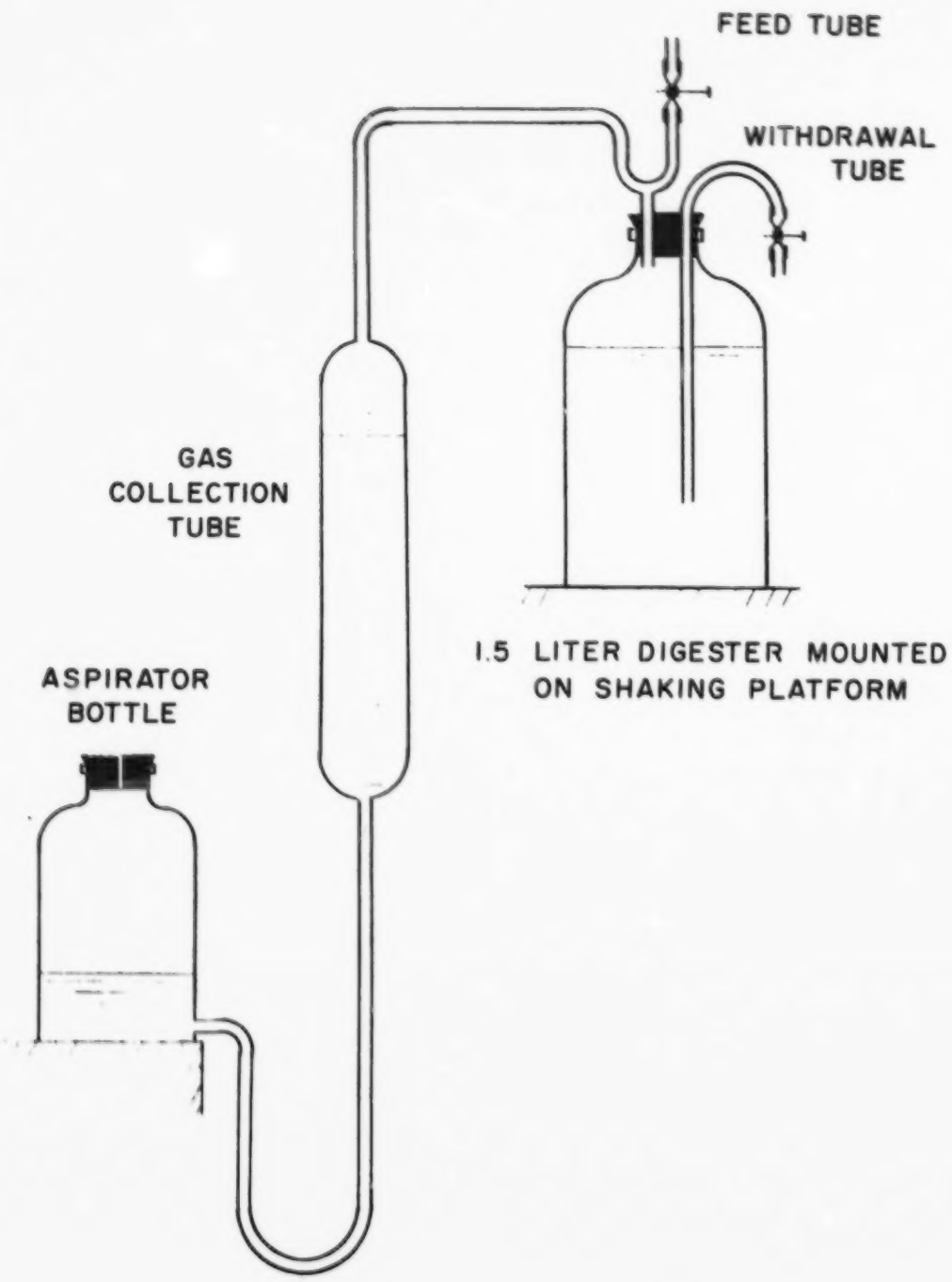


FIGURE 2 - SCHEMATIC LAYOUT OF LABORATORY DIGESTER

TABLE 2

RAW SLUDGE FEED CHARACTERISTICS

Total Solids	1.73 Percent
Volatile Solids	80 Percent of Total
COD	24,000 mg/l
Loading Rate	0.05 lb V.S./day/ft^3

To establish equilibrium operating conditions, the nine digesters used in this study were operated for 60 days prior to the beginning of the heavy metal additions. One digester served as a control and received only raw sludge feed. The other eight digesters received an aliquot of heavy metal salt solution which was added daily along with the raw sludge feed. The metals were fed as the soluble sulfate salts. This procedure was followed to simulate expected field operation in which heavy metals would be added to the digester with the raw sludge, and subsequently be precipitated by sulfides formed from reduction of the sulfates within the digester. The sulfide salts of the heavy metals could have been added, but it was felt this would not have simulated expected field conditions of operation as well. Addition of the sulfate salts instead of sulfide salts also allowed for the possibility that the heavy metals may preferentially form complexes or precipitates with materials in the digester other than sulfide, thus altering the possible toxic effects.

Initially, each of the four metals studied was fed at two different concentrations to separate digesters. The concentrations of the added heavy metal sulfates were 6.25 and 12.5 mM, which would require the equivalent of 200 mg/l and 400 mg/l of sulfur, respectively, for precipitation. The corresponding concentrations of each of the heavy metals added are shown in Table 3.

TABLE 3

HEAVY METALS ADDED TO FEED OF INDIVIDUAL DIGESTERS

Digester	Heavy Metal	Salt Added	Concentration in Feed		
			mM	mg/l S	mg/l Metal
1	Copper	$CuSO_4 \cdot 5H_2O$	6.25	200	397
2	Copper	$CuSO_4 \cdot 5H_2O$	12.5	400	794
3	Zinc	$ZnSO_4 \cdot 7H_2O$	6.25	200	409
4	Zinc	$ZnSO_4 \cdot 7H_2O$	12.5	400	817
5	Nickel	$NiSO_4 \cdot 6H_2O$	6.25	200	367
6	Nickel	$NiSO_4 \cdot 6H_2O$	12.5	400	734
7	Iron	$FeSO_4 \cdot 7H_2O$	6.25	200	349
8	Iron	$FeSO_4 \cdot 7H_2O$	12.5	400	698

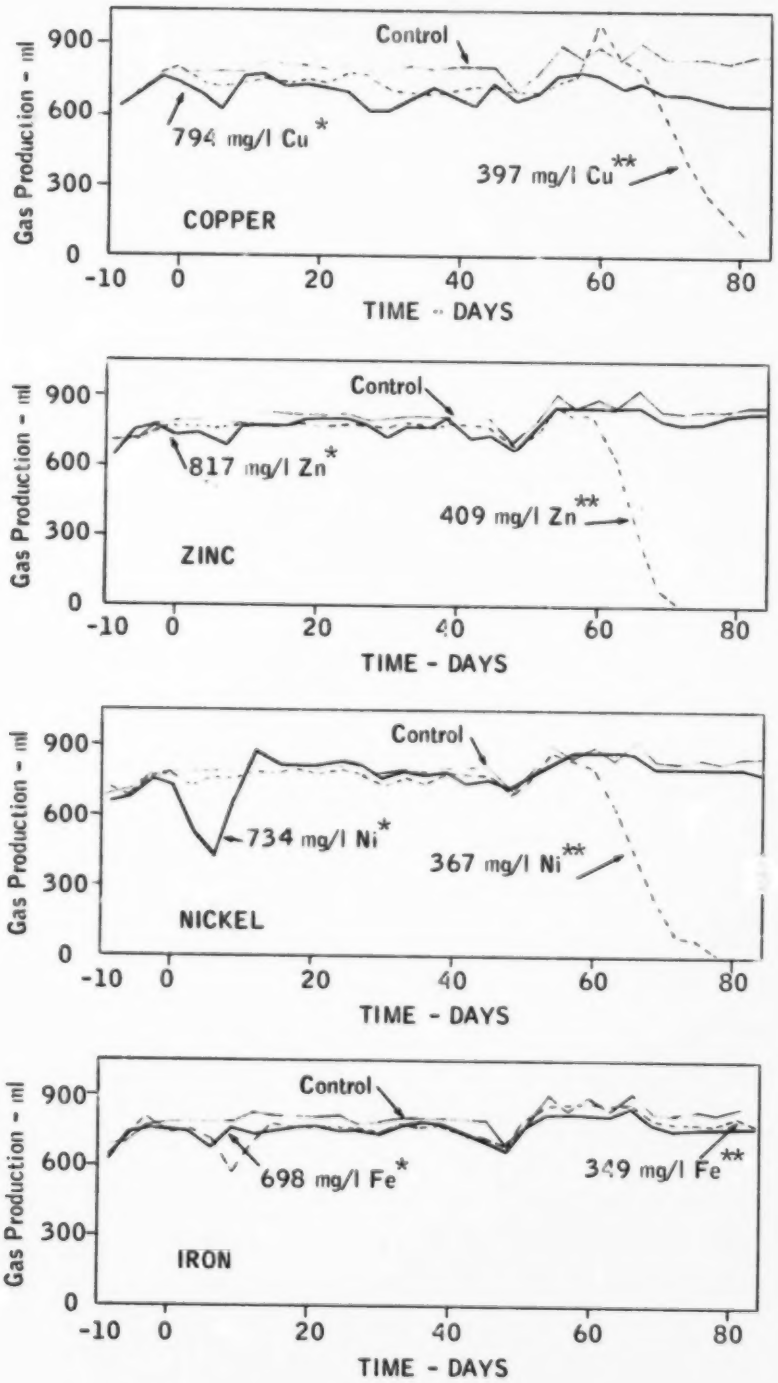
When the digesters had been operated successfully for an extended period of time with daily addition of heavy metal sulfates, metal chloride salts were substituted for the sulfate salts in the 6.25 mM series. With this change, no sulfates were available for reduction to sulfides and so complete sulfide precipitation of the heavy metals could no longer take place. This allowed an observation of the toxic effects of the metals in the absence of sulfides. After this series of experiments, the effect of various combinations of the four metals on anaerobic treatment was studied in a similar manner. Procedures unique to the operation of each digester are described in more detail in the results section.

The aliquots of digester contents withdrawn daily were frequently subjected to routine analyses for process control. Analyses performed were pH, alkalinity, total volatile acids by column partition chromatographic technique,[15] total and volatile solids, and digester gas analysis by gas chromatography. Total and soluble sulfides were determined according to the titrimetric method for sewage,[16] using a 25-ml sample. For soluble sulfides, the samples were placed immediately after collection into centrifuge tubes containing 0.1 ml each of 6 N $AlCl_3$, and 6 N NaOH. The completely filled tubes were stoppered and centrifuged for five minutes at low speeds (4 to 5 x 10^3 rpm). A 25-ml volume of the centrifuged supernatant liquor was subjected to the recovery technique employed for total sulfides. The sulfide recovery efficiency, exclusive of the centrifugation step, was found to be in the 90 to 100 percent range as determined from a series of known Na_2S solutions having sulfide concentrations as S of 0 to 1,100 mg/l. Sulfides in the digester waste gas were determined by expelling a measured volume of the collected gas through a zinc acetate solution, and then proceeding with the iodine-thiosulfate back titration. All sulfide values presented are as directly measured.

EXPERIMENTAL RESULTS

Individual Heavy Metals

Presented here are the results of the addition of the sulfate salts of copper, zinc, nickel, and iron, individually to separate digesters in concentrations equivalent to 200 mg/l and 400 mg/l sulfur. The effects of these additions on gas production are shown in Figure 3. The additions of heavy metals were continued for 57 days, corresponding to approximately 3 detention times. Throughout this period, the operation of all digesters proceeded quite satisfactorily, with gas production approaching that of the control. Initially, however, the unit receiving 734 mg/l of nickel appeared to be affected as evidenced by a decrease in gas production. This retardation may have been due to incomplete reduction of sulfates. The condition was soon relieved and digestion then proceeded normally in this unit also.



* Added as Sulfate Salt During Period Shown.

** Changed from Sulfate Salt to Chloride Salt on Day 57.

Figure 3 - Gas Production for Digesters Receiving Individual Heavy Metals

In all cases, the volatile acid concentrations were low (less than 100 mg/1) and percent of methane in the digester gases was normal, (63 to 67 percent). In almost all units, the digestion in the presence of heavy metals was the same as in the control. The sole exceptions were the units receiving copper. Here, the total gas production remained slightly below that of the control. This was especially noticeable in the unit receiving 794 mg/1 of copper. Apparently the copper at this concentration caused some minor effects, although such effects were not revealed by the normal routine analyses.

As will be indicated later, the sulfates appeared to be reduced to sulfides, which then precipitated the heavy metals. Thus, the heavy metals were rendered non-toxic. To further verify that the sulfides were essential in the reduction of toxicity, the sulfate additions to the units receiving 200 mg/1 as equivalent sulfur, were discontinued after 57 days of operation. In these units the heavy metals were then added as the chloride salts. The units receiving the higher concentration of heavy metal sulfate salts were continued and served as controls. Figures 3 and 4 show that the copper, zinc, and nickel digesters failed within a very short time after the sulfate salts were replaced by chloride salts. Gas production in all cases dropped almost to zero within 10 to 20 days. However, the unit receiving iron was unaffected by this change. Thus, it appears sulfides are required to prevent toxicity from the heavy metals, copper, zinc, and nickel.

The change in gas production and volatile acid concentration which occurred after the sulfate additions were discontinued are shown in Figure 4. Here it can be seen that gas production was the initial parameter affected by the heavy metal toxicity. The volatile acid concentration began to rise only after the gas production was noticeably reduced. This was especially true in the unit receiving nickel. Here, the gas production was reduced to about 20 percent of the control before a noticeable increase in volatile acids occurred. Also, when gas production

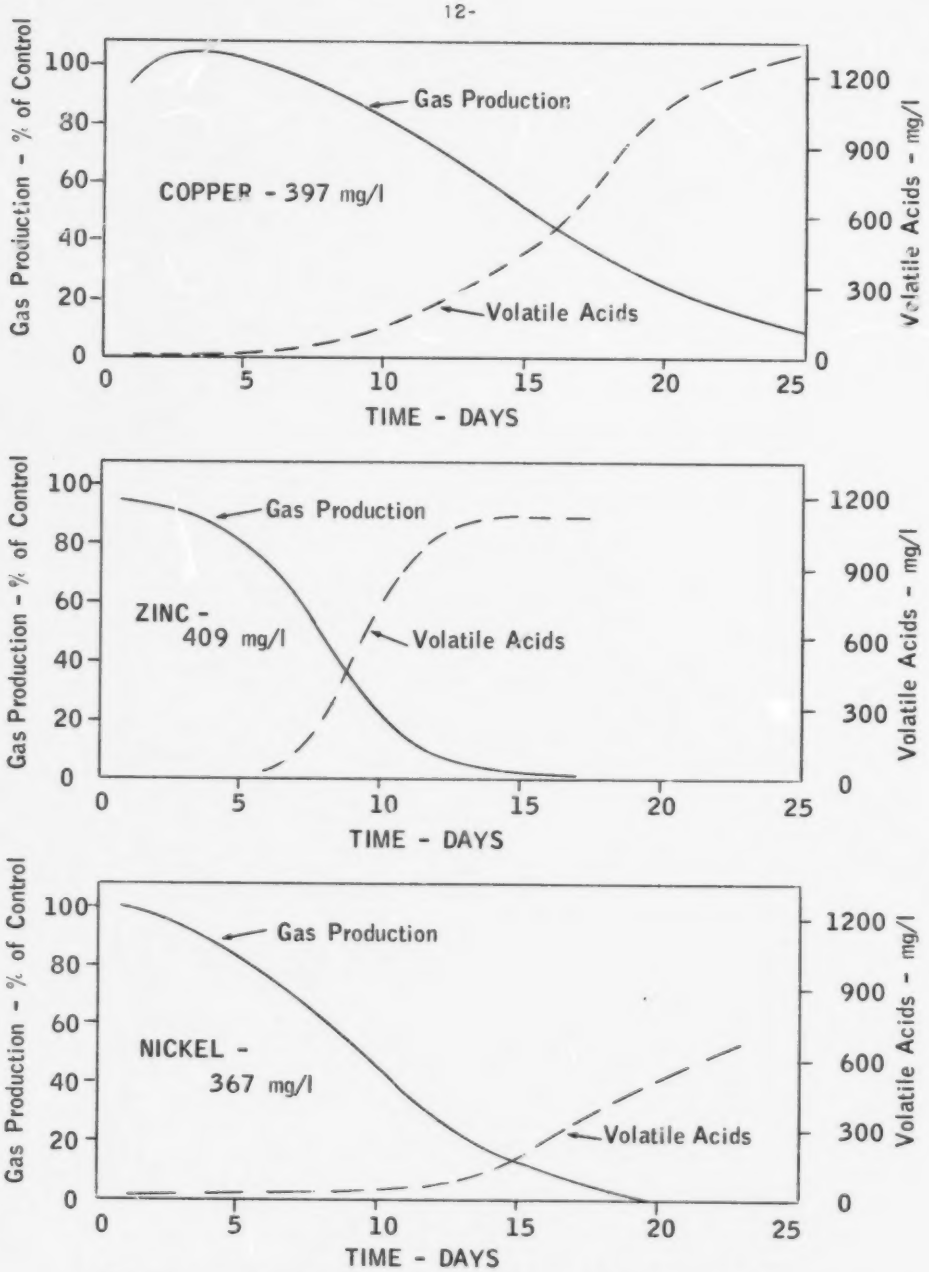


Figure 4 - Gas Production and Volatile Acid Concentration for Digesters Receiving Metals as Shown for Time Period Beginning at Termination of Sulfate Addition

reached zero, the volatile acid concentration was only 500 mg/l. With zinc and copper, the final volatile acid concentration after complete failure of digestion, was only about 1,000 mg/l. Based on these observations, it appears the heavy metals affect the acid producing bacteria, at least as much if not more than the methane bacteria. It is evident here that an increase in volatile acids is not a reliable indicator of the onset of heavy metal toxicity. By the time volatile acid concentration had risen significantly, the digesters had already been seriously affected. This is another indication that all normal control parameters, rather than one alone, should be measured for adequate digester control.

One other parameter sometimes used to judge digester operation is gas analysis. It has often been noted that when digesters begin to fail, the percentage of methane decreases significantly. The change in methane fraction which occurred after significant changes in gas production occurred in this study are shown in Table 4.

TABLE 4

EFFECT OF HEAVY METAL TOXICITY ON METHANE FRACTION OF GAS

Heavy Metal	Days After Change To Chloride Salt	Gas Production in % of Control	% Methane in Gas
Copper - 397 mg/l	13	69	60
	20	24	50
Zinc - 409 mg/l	5	83	67
	13	5	50
Nickel - 367 mg/l	5	81	67
	13	22	67

The changes in methane fraction were small, and were not noticeable until gas production had dropped significantly. In the unit receiving nickel no change in methane percentage was noted even when gas production was only 22 percent of the control. The relatively small changes in methane percentage which accompanied the large decrease in gas production again indicates the microorganisms responsible for hydrolysis of complex organics to organic acids were as much or more seriously affected by heavy metals than the methane forming bacteria.

Combinations of Heavy Metals

In the next phase of this study, combinations of heavy metal sulfate salts were introduced to digesters. The digesters which had been receiving the higher concentrations of heavy metal sulfate salts in the individual heavy metal study above were continued in operation and switched to combinations of heavy metals for this phase. The metal combinations were chosen to give a total concentration of 12.5 mM heavy metals in the feed. The concentrations of each heavy metal used are shown in Table 5. Figure 5 shows the daily gas production resulting from the daily additions of these combinations.

The first graph shows the gas production from the copper-zinc combination which was added to the unit previously receiving 12.5 mM of copper. It can be seen that once this combination was added, gas production improved, and was then as good as in the control. Thus, with this combination, the slightly detrimental effect noted with copper alone appeared to be relieved. At the end of 31 days of satisfactory operation, the sulfates were removed from the daily feed and chloride salts of the heavy metals added. As in the previous study, this change resulted in rapid failure of the digester.

The zinc-nickel combination proceeded normally for 31 days, with gas production similar to the control. After that time, the sulfates were removed and the digestion failure was rapid, with gas production reaching zero within about 12 days.

TABLE 5

CONCENTRATIONS OF HEAVY METALS IN FEED SLUDGE FOR COMBINATION STUDY

Heavy Metals	Concentration of Heavy Metals	
	mM	mg/l
Copper-Zinc Unit:		
Copper	6.25	397
Zinc	6.25	409
Total	12.5	806
Zinc-Nickel Unit:		
Zinc	6.25	409
Nickel	6.25	367
Total	12.5	776
Iron-Zinc Unit:		
Iron	6.25	349
Zinc	6.25	409
Total	12.5	758
Copper-Nickel-Zinc Unit:		
Copper	4.16	265
Nickel	4.16	244
Zinc	4.16	272
Total	12.5	781

The combination of copper, zinc and nickel gave results similar to the other metal combinations. Gas production was normal as long as sulfates were included with the daily feed. When the sulfates were removed, gas production rapidly decreased and total failure resulted.

The last graph shown in Figure 5 is the result of the iron-zinc combination. In this study it was reasoned that since iron alone was not detrimental even without sulfides, sulfides should not be required for the iron, but only for the zinc. Thus, only enough sulfides

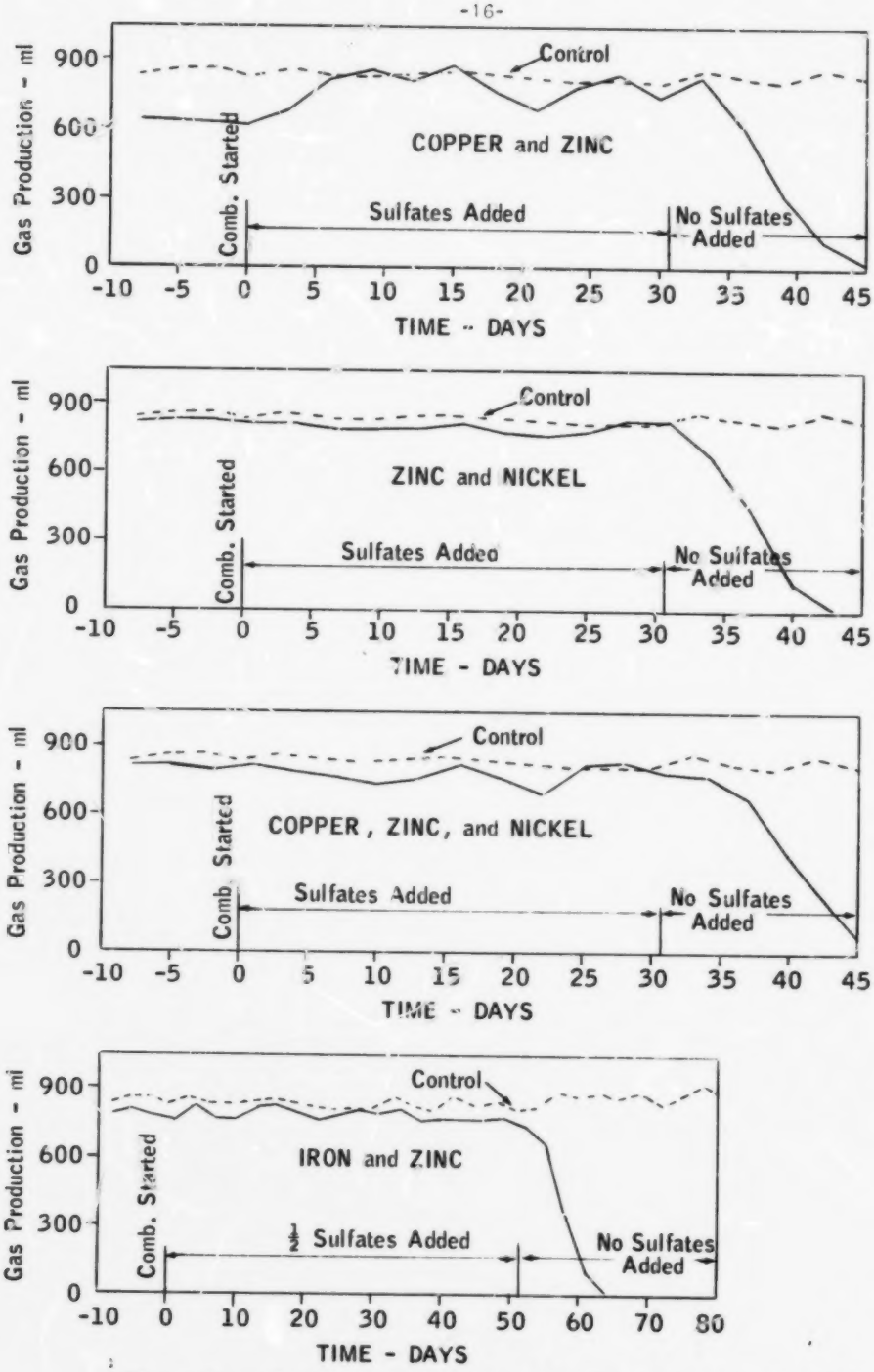


Figure 5 - Daily Gas Production for Digesters Receiving 12.5 mM Concentration of Combination of Heavy Metals

need be present to precipitate the added zinc. Table 1 indicates that zinc sulfide is much more insoluble than ferrous sulfide, and so should precipitate first. To see if this would be the case, only zinc was added as the sulfate salt, while iron was added as the chloride salt.

From Figure 5, it can be seen that addition of sufficient sulfate or sulfide precursor to precipitate only the zinc was sufficient to maintain normal digester operation. Such operation was continued for 52 days. At that time, all sulfate additions were discontinued and then rapid digestion failure occurred. As in all preceding cases, digester pH and alkalinity remained normal during failure.

Figure 6 shows the gas production and volatile acids concentration which resulted when sulfates were removed from the copper-zinc digester, as well as the zinc-nickel digester. Again, it can be seen that gas production decreased significantly before the volatile acid concentration began to increase. Complete failure occurred before the volatile acid concentration reached 1,000 mg/l. It is also interesting to note that again, in the digester receiving nickel, the gas production was almost zero before the volatile acid concentration began to increase. When complete failure was apparent, the volatile acid concentration had only reached about 300 mg/l. It thus appears that nickel is extremely toxic to the organisms producing volatile acids and that with this metal, complete failure could occur with practically no indication of this failure being given by a volatile acid concentration change.

Table 6 shows the changes in gas composition which occurred during failure of two of the combination digesters. This represents the changes which occurred after sulfates were removed from the daily feed. As with the study on individual metals, the percentage of methane in the gas remained practically the same throughout the failure of the digestion process.

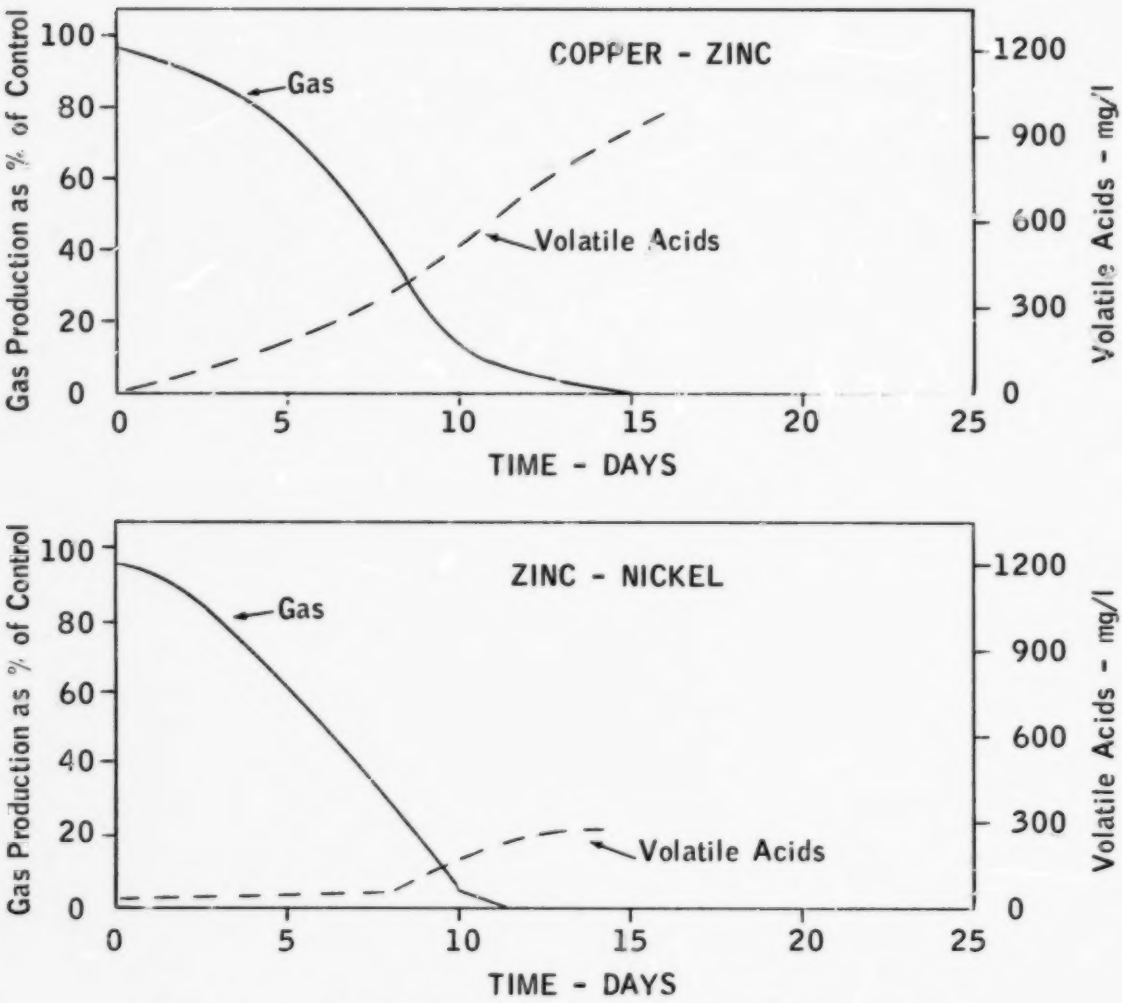


Figure 6 - Gas Production and Volatile Acid Concentration for Digesters Receiving Combinations of Metals as Shown for Time Period Beginning at Termination of Sulfate Addition

TABLE 6

EFFECT OF TOXICITY FROM COMBINATION OF HEAVY METALS ON METHANE FRACTION OF GAS

Heavy Metal Combination	Days After Change to Chloride Salt	Gas Production in % of Control	% Methane in Gas
Copper-Zinc	1	91	65
	8	39	64
Zinc-Nickel	1	91	64
	8	29	66

For these combinations as well as for the individual nickel failure, change in gas composition could not have been used as an indicator of impending failure. Thus, two of the common parameters used as indicators of impending failure would have been of little value here.

Measured Sulfide Concentrations

The sulfide concentrations measured in the various digesters during operation are of interest to indicate the extent of sulfate reduction obtained. Figure 7 indicates the concentrations of total and soluble sulfides in the liquor, and sulfides in the gas in the digesters fed individual metal sulfates at a concentration of 400 mg/l as equivalent sulfur. The total sulfide concentration in the digesters receiving zinc and iron was close to 400 mg/l, corresponding to the quantity of sulfur introduced to the digesters. The concentrations started out low when introduction of the heavy metals and sulfates were first initiated and reached close toequilibrium concentrations after about 40 to 60 days of operation.

The measured total sulfide concentration for the copper and nickel units, however, never exceeded that of the control, since the sulfides of copper and nickel are non-acid labile and are not measured in the standard sulfide test. Analysis indicated sulfates were absent in these units; thus, the sulfates were apparently reduced to sulfides although the normal test for sulfides will not indicate this. The sulfide recovery with the zinc sulfide was close to 100 percent, while that for iron was slightly below this. Between days 30 and 55, the total sulfide concentration in the iron unit increased erratically, and then decreased back to normal. No adequate explanation for this unusual rise was apparent.

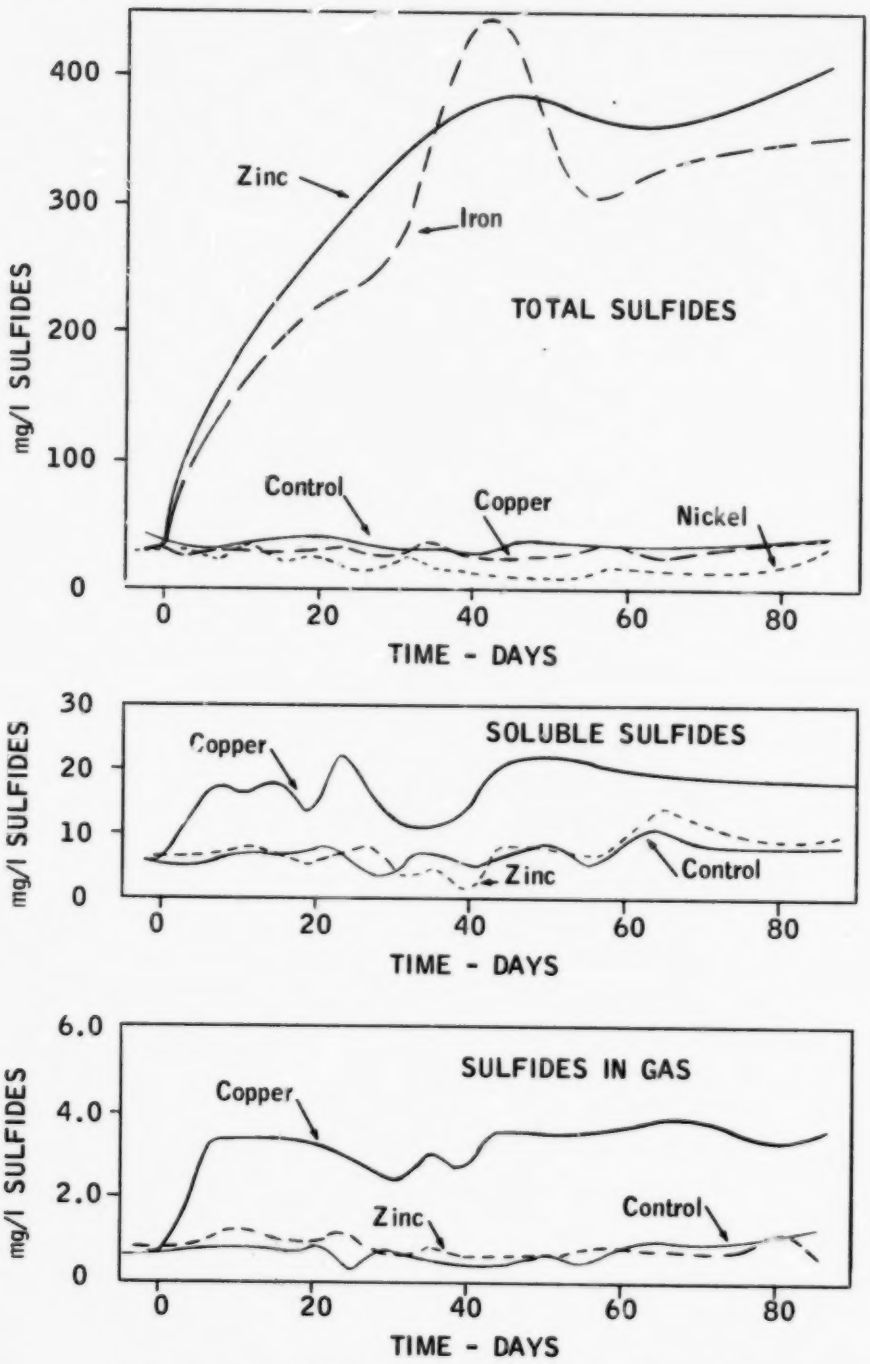


Figure 7 - Various Forms of Sulfides in Digesters Receiving 400 mg/l Sulfate Sulfur with Individual Metal Salts

The graph for soluble sulfides indicates a peculiarity with copper. All the metal-containing units except the copper-containing one had a soluble sulfide concentration similar to that of the control. The soluble sulfide concentration for the zinc unit is shown in Figure 7 to indicate this. However, the copper unit had a much higher soluble sulfide concentration. It is possible that some of the cupric copper was reduced to cuprous copper in the digester, which would stoichiometrically require less sulfides for precipitation. Thus, the additional sulfides would be released as soluble sulfide as shown.

The last graph in Figure 7 indicates sulfide concentration in the gas. The high concentration of sulfide in the gas in the copper unit is what would be expected, due to the higher soluble sulfide concentration as indicated above. The sulfides in the gas in all other metal-containing units were similar to that of the control as indicated by the graph for the zinc-containing unit.

Effect of High Iron Concentration

Since ferrous iron was found to be non-toxic to digestion, even in the absence of sulfides, it was desired to determine if there was a practical upper limit to the quantity of iron which could be added. In this study, a ferric compound rather than a ferrous compound was used. Initially, a ferric chloride solution was added along with the daily feed to give a concentration of 698 mg/l iron. This addition was continued for 72 days. As shown in Figure 8, the gas production was only slightly affected by this concentration. After day 72, the concentration of ferric chloride was doubled to give a concentration of iron in the feed of 1,396 mg/l. This addition was continued for 32 days. Figure 8 indicates that during this time, gas production was affected only slightly. Other digestion parameters were normal during this time. It thus appears from this study that very high concentrations of iron can be tolerated in anaerobic digestion, providing the iron is added continuously on a daily feed basis, rather than being added on a slug basis.

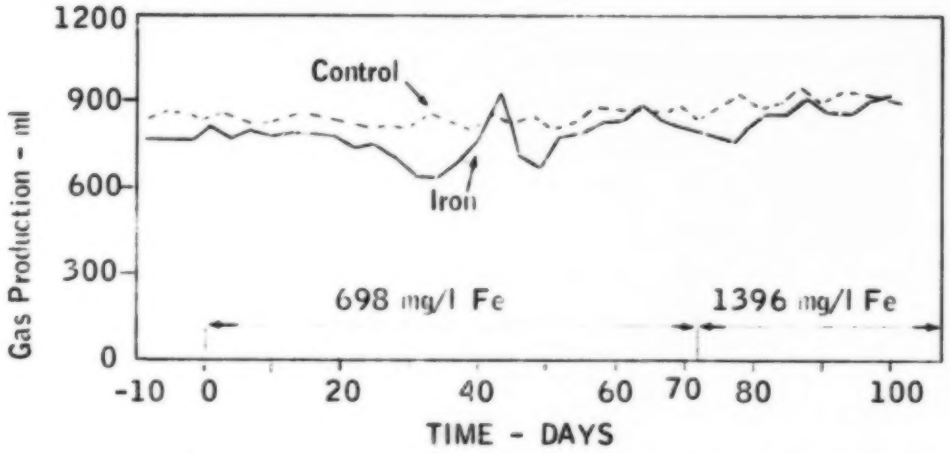


Figure 8 - Daily Gas Production for Digester Receiving Iron Fed as $FeCl_3$

The tolerance of anaerobic digestion for iron is probably related to the fact that (1) iron is not very toxic, and (2) precipitation of iron as the hydroxide by hydrolysis is sufficient at normal digester pH ranges, so that only a low, non-toxic concentration of iron will remain in solution. One point that should be noted is that during hydrolysis of iron, the pH in the digesters decreased. Such decrease in pH had to be controlled by addition of more buffering materials.

DISCUSSION

General

The results of this study indicate that sulfides play a significant role in preventing toxicity of most heavy metals in anaerobic treatment. In this study, sulfides formed by the biological reduction of sulfates effectively prevented copper, zinc, and nickel, both singly and in combination, from exerting toxic effects on anaerobic treatment. In the case of metals added individually, the importance of sulfides was demonstrated by the contrast between (1) the rapid and severe toxic effects on digestion occurring in units receiving heavy metals when the addition of an equivalent amount of sulfate was terminated and (2) the satisfactory digestion occurring in parallel units receiving twice the concentration of metals as the above units and an equivalent amount of sulfate. Correspondingly for addition of combinations of the three metals studied, no toxic effects were noted as long as an amount of sulfate equivalent to the total metal concentration was supplied. Again, when sulfate addition was terminated, rapid toxicity occurred. Thus, it appears that sulfate reduction can go on in the presence of heavy metals and that the role of the sulfide formed is the removal, most probably by precipitation, of the metal ion from the soluble phase of the digester, and hence the biological environment.

The results of this study support the findings of Masselli et al[1] concerning the use of sulfide to prevent the toxicity of copper and extend the applicability of the technique to include nickel and zinc. Similar success would probably be achieved with most other heavy metals, since they form insoluble sulfide salts. The other metal studied here, iron, proved

to be non-toxic in anaerobic treatment even without the addition of a sulfide precursor when added daily in high concentrations. As a consequence of this finding, it is felt that it is not necessary to consider iron in evaluating the possibility of heavy metal effects on anaerobic waste treatment. Further significance of this finding regarding iron will be discussed later.

Significance of Reported Concentrations

As noted previously in the reported literature, the toxic concentrations of heavy metals, notably copper, have varied widely. Table 7 shows the concentrations of heavy metals in the digesters after 70 days of metal addition in the 12.5 mM series of this study. The units were operating satisfactorily with metal concentrations well over 10 percent of the volatile solids concentration, which is much higher than any previous study noted. The digesters operated well because the heavy metals were precipitated by sulfides formed from sulfate reduction. Variations in toxic levels of heavy metals noted by others are no doubt due to variations in the quantities of sulfides present in the digesters for such heavy metal precipitation.

It is also significant to point out that the sum total concentration of the heavy metals present in any given situation is the important parameter rather than the concentration of each individual metal. Toxicity will result when the total equivalent concentration of the toxic heavy metals exceeds the equivalent concentration of sulfides present for precipitation. Thus, any study of possible heavy metal toxicity should include determinations of all heavy metals, as well as the total concentration of sulfides available for precipitation. Such a study need not include iron, however, since iron is one of the most soluble of the heavy metal sulfides, as well as being non-toxic. Thus, the sulfides formed during digestion would be available first for precipitation of the toxic heavy metals, and only then would iron be precipitated. Also, sulfide bound as iron sulfide would constitute a sulfide reservoir available for precipitation of more toxic and more insoluble sulfide forming heavy metals.

TABLE 7

CONCENTRATION OF HEAVY METALS IN DIGESTERS 70 DAYS AFTER BEGINNING OF METAL ADDITIONS

Metal Added	Metal Conc. in Feed mg/l	Digested Sludge Concentration		Metal Concentration in Digesters (Calculated)		
		Total Solids - %	Volatile Solids % of Total	mg/l	% of Total Solids	% of Volatile Solids
Control	0	0.828	57.4	---	---	---
Copper	794	1.02	57.1	772	7.6	13.3
Zinc	817	0.904	51.3	795	8.8	17.2
Nickel	734	0.871	53.7	713	8.2	15.3
Iron	698	0.815	53.0	679	8.4	15.7

Control of Heavy Metal Toxicity

This study, as well as that of Masselli, Masselli, and Burford,[1] has shown that the toxic effects of heavy metals can be relieved by precipitation with sulfide; thus a relatively easy procedure is available for heavy metal control. If heavy metals are the cause of digester upset, the addition of an excess of sulfides will relieve the problem. Such an addition can also be made if heavy metal toxicity is only suspected. If the inhibition is then relieved, the suspicions would be fairly well confirmed.

The quantity of sulfide required is approximately 1/2 mg/l for each mg/l of the toxic heavy metal present. Since digesting sludge normally contains a relatively high sulfide concentration, only sufficient additional sulfides need be added to control the excess heavy metals not already precipitated. Since soluble sulfides can be quite corrosive and high concentrations can also be toxic,[17] excessive quantities should be avoided. Such problems might be minimized by adding an iron-containing compound along with the sulfides. This would allow retention of the sulfide in the digester in a non-toxic insoluble form, which would still be available for reaction with other heavy metals as explained previously.

City of Palo Alto Experience

The City of Palo Alto, California, has a 3/4 million gallon anaerobic digester treating combined primary and trickling filter municipal waste sludge. This digester has operated with frequent severe upsets over the past several years, and heavy metals were suspected by the plant personnel as the cause because of the large number of electronic firms with plating operations connected to the municipal sewer system. A survey conducted by Jenks and Jenks, Consulting Sanitary Engineers, indicated the digesting sludge contained over 200 mg/l of zinc, almost 100 mg/l each of copper and lead, and a total toxic heavy metal concentration of over 500 mg/l. The control of this problem was attempted by the plant personnel in July, 1963, when 25 pounds of technical grade sodium sulfide costing only a few dollars was added to the digester after the volatile acid concentration had increased from a normal value of about 200 mg/l to between 500 and 600 mg/l. Previous failures had been

preceded by a similar rise in volatile acids. However, this time the addition of only a few mg/l of sulfides was followed by return of digester operation to normal. This control procedure has been applied two times since and each time treatment conditions have returned to normal. Sometimes a second addition of sulfides was required within one week before completely satisfactory operation was obtained.

Although it cannot be certain without control tests whether or not the sulfides added were responsible for the return to satisfactory operation, the circumstantial evidence strongly indicates this was the case. It is a simple matter to add sulfides if heavy metal toxicity is suspected. Such addition may prevent the occurrence of a potentially severe problem, and one for which the cause is difficult to confirm even when extensive analyses are conducted. Here, a few pounds of sulfides added for prevention may be worth many dollars and man hours spent for the cure of a "stuck" digester.

SUMMARY AND CONCLUSIONS

The role of sulfide in preventing heavy metal toxicity has been studied by the operation of a series of laboratory digesters receiving daily additions of the heavy metals, copper, zinc, nickel, and iron, and a sulfide precursor. The experimental results have been discussed with regard to significance of individual and total metal concentrations, methods of reporting heavy metal concentrations, mechanism of detoxification and control procedures. The following conclusions can be drawn from this study:

1. Soluble copper, zinc, and nickel heavy metal salts are toxic to anaerobic treatment.
2. Exceptionally high concentrations of iron can be tolerated in anaerobic treatment, if added daily along with the feed.
3. Under anaerobic conditions, most toxic heavy metals can be precipitated and rendered non-toxic in the presence of an equivalent concentration of sulfides.
4. The sum total concentration of toxic heavy metals which can be tolerated is directly related to the quantity of sulfides present for their precipitation.
5. The addition of sulfide or sulfide precursors has allowed the presence of greater than 10 percent of heavy metals on a dried volatile solids basis without inhibiting the digestion process.
6. The addition of sulfides or sulfide precursors to relieve heavy metal toxicity is a sound control procedure.

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